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PATENT SPECIFICATION



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545,838

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COMPLETE SPECIFICATION

Improvements in or relating to the Vulcanisation of Rubber

We, E.I. DU PONT DE NEMOURS AND Co.,
of Wilmington, Delaware, United States
of America, a corporation organised and
existing under the laws of the State of
Delaware, United States of America, do
hereby declare the nature of this invention
and in what manner the same is to be
performed, to be particularly described
and ascertained in and by the following
10 statement:

This invention relates to the vulcanisation
of rubber and more particularly to
accelerators for the vulcanisation of
rubber.

15 The general use of 2-mercaptopthiazoline
as an accelerator of vulcanisation is
known. The use of secondary accelerators
to activate the cure, obtainable with a
primary accelerator, is also known. It
20 has generally been found, however, that
it is impossible to use a secondary
accelerator, such as an aldehyde-amine or
a guanidine, with an acidic primary
accelerator such as 2-mercaptopbenzothia-
25 zole, because of the great activity of the
combinations at processing temperatures.
Secondary accelerators have been used
successfully, however, with derivatives of
2-mercaptopbenzothiazole, for example, a
30 guanidine has been used with the benzyl
ester of 2-mercaptopbenzothiazole.

An object of this invention is to provide
vulcanised rubber of improved properties,
by employing as accelerators, in the
35 vulcanisation process, a new combination
of accelerators which are sufficiently safe
at processing temperatures for commercial
utilisation and which are at the same time
very active at normal vulcanisation tem-
40 peratures.

According to the present invention we
incorporate in a rubber stock, prior to
vulcanisation, a small proportion of a
45 combination of primary and secondary
accelerators, in which the primary
accelerator is 2-mercaptopthiazoline or a
carbon substituted 2-mercaptopthiazoline
carrying as substituents one or more
50 alkyl and/or hydroxyalkyl groups bonded
to the ring carbon atoms of the thiazoline
ring, and the secondary accelerator is
an aldehyde-amine, arylguanidine and
thiuram sulphide accelerator. We have

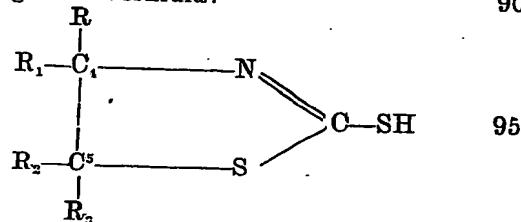
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found that such combinations of
primary and secondary accelerators are
sufficiently safe at ordinary processing
temperatures to permit their use com-
mercially, that is, such combination of
accelerators does not tend to cause scorching
or prevulcanisation to an objectionable
extent so as to make their use impractical
commercially. At the same time, such
combination of accelerators show maxi-
mum activity at the usual vulcanising
temperatures, and produce vulcanisates of
high tensile strength and moduli.

We have found that the best results are
obtained with 2-mercaptopthiazoline itself
as a primary accelerator. Of the carbon
substituted 2-mercaptopthiazolines, those
in which the substituents are alkyl groups
are generally preferred and we particularly
prefer those in which the alkyl groups are
lower alkyl groups, that is, contain from
one to six carbon atoms.

By the term "alkyl" we mean aliphatic
radicals consisting of carbon and
hydrogen. By the term "hydroxyalkyl"
we mean aliphatic radicals, which, except
for the hydroxy group, consist of carbon
and hydrogen. By the term "carbon
substituted 2-mercaptopthiazolines" we
mean those in which the substituents are
directly bonded to the ring carbon atoms
of the thiazoline ring, that is, those in
which the substituents are in the 4 or 5
or both the 4 and 5 positions.

The compounds employed as primary
accelerators in the present invention have
the general formula:



wherein R, R₁, R₂ and R₃ represent
hydrogen or an alkyl or an hydroxyalkyl
group.

While any of the aldehyde-amine,
arylguanidine and thiuram sulphide
accelerators may be employed, we pre-
ferably employ the aldehyde-amine

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accelerators, and particularly butyraldehyde-aniline, known to the trade as "Accelerator 808". Of the arylguanidine accelerators, we prefer di-o-tolylguanidine 5 and diphenylguanidine. Of the thiuram sulphide accelerators, we preferably employ tetramethylthiuram monosulphide and tetramethylthiuram disulphide.

The combination of accelerators, 10 employed in accordance with our invention, generally comprises from about 1 to 50 parts of the primary accelerator for each part of the secondary accelerator. When the secondary accelerator is an arylguanidine, it will generally be preferred to employ from about 1.5 to about 10 parts of the primary accelerator for each part of the arylguanidine. When an

aldehyde-amine is employed as a secondary accelerator, it will generally be preferred to employ from about 2 to about 10 parts of the primary accelerator to each part of the aldehyde-amine. When a thiuram sulphide 70 is employed as a secondary accelerator, it is preferred generally to employ from about 20 to about 50 parts of the primary accelerator to each part of the thiuram sulphide.

In order to show the safety of these combinations at the processing temperatures with the desirable properties obtainable at vulcanising temperatures, the following stocks were prepared. The base stock used in these tests is essentially the base stock of a modern inner tube. 75 80

	Stock	A	B	C	D
	Smoked sheets	100	100	100	100
25	Zinc oxide	5	5	5	5
	Finely divided whiting	25	25	25	25
	Stearic acid	1.5	1.5	1.5	1.5
	Sulphur	2	2	2	2
	2-Mercaptobenzothiazole	0.75	—	0.75	—
	2-Mercaptothiazoline	—	0.75	—	0.75
30	Di-o-tolylguanidine	0.15	0.15	—	—
	Butyraldehyde-aniline	—	—	0.1	0.1

Stocks A and C, in which 2-mercaptopbenzothiazole is used as the primary accelerator, were run for purposes of comparison with corresponding stocks B and

D in which 2-mercaptothiazoline is used as the primary accelerator. The results of the vulcanisation tests on these stocks 95 are given in Table I.

TABLE I.

	Minutes Cured	Temp.	Stock A 500% Tensile	Stock B 500% Tensile	Stock C 500% Tensile	Stock D 500% Tensile
40	60	227	1375	4300	350	1275
45	45	287	1175	3500	1050	4000
	60	287	1025	3025	975	3575

These results show (Stocks A and B) 50 that, when di-o-tolylguanidine is used as the secondary accelerator, the stock (Stock B), in which 2-mercaptothiazoline is used as the primary accelerator, is very much safer than the one (Stock A), in which 2-mercaptopbenzothiazole is used as the primary accelerator. It shows, in the 60 minutes cure at 227° F., a modulus at 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 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combinations.

In order to show that the results obtained above are not limited to the particular test formula used, the following stocks were prepared.

	Stock	E	F	G
10	Smoked sheets	- - 100	100	100
	Zinc oxide	- - 5	5	5
	Channel black	- - 25	25	25
	Stearic acid	- - 3	3	3
	Sulphur	- - 3	3	3
15	2-Mercaptothiazoline	- 0.9	0.97	0.9
	Di-o-tolylguanidine	- 0.9	—	—
	Tetramethylthiuram monosulphide	- —	0.03	—
20	Butyraldehydeaniline	- —	—	0.1

These stocks were cured for 30, 45, 60 and 90 minutes at 274° F. and the following test data were obtained.

25

TABLE II.

Minutes cured at 274° F.	Stock E		Stock F		Stock G	
	500% Tensile		500% Tensile		500% Tensile	
30	30	2300	4700	2450	5025	2375
	45	2700	5125	2875	4925	2775
	60	3075	4925	3000	4450	3025
	90	3275	4375	3275	4400	3275

35

There was no difficulty in processing any of these stocks, but, as is shown in the table, when they were cured at 274° F., stocks having very high moduli and tensile strength were obtained.

When accelerating with a combination of accelerators, it is generally customary to use one, the primary accelerator, in much larger amounts than the other, the secondary accelerator or accelerator activator. Under these conditions, the properties of the vulcanisate more nearly approach the properties of a vulcanisate prepared from the primary accelerator alone than they do the properties of a vulcanisate prepared from the secondary accelerator alone. For example, vulcanisates prepared from the guanidines alone are well-known to be very susceptible to rapid deterioration on ageing, i.e. they are poor "ageing" stocks. On the other hand, vulcanisates prepared from the thiazoles or thiazole derivatives are well-known to be extremely resistant to deterioration on ageing. When a small amount of a guanidine is used to activate the cure of a thiazole accelerator, the resulting vulcanisate has the age resisting characteristics of the primary thiazole

accelerator. It has been found that vulcanisates, prepared by the combined use of a 2-mercaptothiazoline and a secondary accelerator, such as the guanidines, the aldehyde-amines and the thiuram accelerators, in which the thiazoline is used in a preponderant amount, likewise show characteristics which make them valuable commercial vulcanisates.

Stocks, obtained by this invention, have very good resistance to deterioration, particularly to deterioration on exposure to high temperatures. In order to show this effect, the following stocks were prepared. For purposes of comparison, tests were also made on an activated mercaptobenzothiazole derivative. For this comparison, the zinc salt of mercaptobenzothiazole was used instead of the free mercaptobenzothiazole, since it represents a combination of accelerators which can be handled commercially as contrasted

Stock	Stock E		Stock F		Stock G	
	500% Tensile		500% Tensile		500% Tensile	
Smoked sheets	- - 100		- - 100		- - 100	
Zinc oxide	- - 5		- - 5		- - 5	
Channel carbon black	- - 50		- - 50		- - 50	
Stearic acid	- - 2		- - 2		- - 2	
Pine tar	- - 1.5		- - 1.5		- - 1.5	
Phenyl-β-naphthylamine	- 0.6		- 0.6		- 0.6	
"Thermoflex" A	- 1.4		- 1.4		- 1.4	
Sulphur	- - 3		- - 3		- - 3	
Zinc salt of 2-mercaptobenzothiazole	- 0.5		- 0.5		- 0.5	
2-Mercaptothiazoline	- —		- —		- 0.5	
"Accelerator 808"	- 0.15		- 0.15		- 0.15	

with the activated free mercaptobenzothiazole which is very "scorchy".

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Stock	H	I
Smoked sheets	- - 100	- - 100
Zinc oxide	- - 5	- - 5
Channel carbon black	- - 50	- - 50
Stearic acid	- - 2	- - 2
Pine tar	- 1.5	- 1.5
Phenyl-β-naphthylamine	- 0.6	- 0.6
"Thermoflex" A	- 1.4	- 1.4
Sulphur	- - 3	- - 3
Zinc salt of 2-mercaptobenzothiazole	- 0.5	- —
2-Mercaptothiazoline	- —	- 0.5
"Accelerator 808"	- 0.15	- 0.15

"Thermoflex" A is the trade name of an antioxidant consisting of 50 parts phenyl-β-naphthylamine, 25 parts diphenyl-p-phenylenediamine and 75 parts of 4:4'-dimethoxydiphenylamine.

"Accelerator 808" is the trade name of a butyraldehydeaniline condensation product.

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Stocks H and I were cured for 60 minutes at 267° F. and showed the following tensile properties.

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TABLE III.

Minutes cured at	Stock H	Stock I
5 267° F.	500% Tensile	500% Tensile
60	2900	4375
	3000	4675

10 These stocks were subjected to artificial ageing by suspending in an air oven at 100° C. for two days. After this time, Stock H had a tensile strength of 1925 lbs./sq.in. and an elongation at break 15 of 420% while Stock I had a tensile strength of 2400 lbs./sq.in. and an elongation at break of 440%. Another type of ageing test was run by suspending these stocks in an oxygen bomb at 300 pounds 20 oxygen pressure and at 70° C. After 14 days, Stock H had a tensile strength of 1375 lbs./sq.in. and an elongation at break of 420%, while Stock I had a tensile strength of 1800 lbs./sq.in. and an elongation at break of 460%. These tests show the 25 extremely great resistance to deterioration exhibited by stocks cured with a combination of 2-mercaptopthiazoline and a secondary accelerator.

30 Although certain definite combinations of activating accelerators with 2-mercaptopthiazoline have been shown, those combinations are illustrative rather than limiting. It is also possible to use other 35 guanidines, for example, diphenylguanidine or triphenylguanidine or the derivatives of the guanidines such as diphenylguanidine phthalate or tartrate or the zinc chloride addition 40 products of the guanidines. Other aldehyde-amines, for example, butyraldehyde-butylamine, anhydro formaldehyde-p-toluidine, anhydro formaldehyde-aniline or methylene dianilide may be used.

45 Other thiuram sulphide accelerators, for example, tetramethylthiuram disulphide may also be used in combination with 2-mercaptopthiazoline.

Compounding ingredients and fillers, 50 other than those shown in the test formulæ and in other proportions, may also be used. While the tests have shown only the use of 2-mercaptopthiazoline itself as the primary accelerator, equally good results 55 can be obtained with the use of the carbon substituted 2-mercaptopthiazolines in which

one or both of the hydrogen atoms in the 4 or 5 or both the 4 and 5 positions of the thiazoline ring are substituted by alkyl groups or hydroxy-alkyl groups; such as, 60 for example

- 4-Methyl-2-mercaptopthiazoline
- 4-Ethyl-2-mercaptopthiazoline
- 4-Propyl-2-mercaptopthiazoline
- 4:4-Dimethyl-2-mercaptopthiazoline
- 5:5-Dimethyl-2-mercaptopthiazoline
- 4-Methyl-4-ethyl-2-mercaptopthiazoline
- 4-Methyl-5-propyl-2-mercaptopthiazoline
- 4:4-Dimethyl-5-propyl-2-mercaptopthiazoline
- 4-Isopropyl-5-propyl-2-mercaptopthiazoline
- 4:4-Dimethyl-5-propyl-2-mercaptopthiazoline
- 4-Ethyl-5-propyl-2-mercaptopthiazoline
- 4-Methyl-4-hydroxymethyl-2-mercaptopthiazoline
- 4-Methyl-4-ethyl-5-propyl-2-mercaptopthiazoline
- 4-Ethyl-5-methyl-2-mercaptopthiazoline
- 4-Propyl-5-propyl-2-mercaptopthiazoline

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the vulcanisation of rubber, characterised in that there is incorporated in the rubber mix, prior to vulcanisation, a small proportion of a combination of primary and secondary accelerators in which the primary accelerator is 2-mercaptopthiazoline or a carbon substituted 2-mercaptopthiazoline carrying as substituents one or more alkyl and/or hydroxy-alkyl groups, and the secondary accelerator is an aldehyde-amine, an arylguanidine or a thiuram sulphide, there being from about 1 to about 50 parts of the primary accelerator 100 to each part of the secondary accelerator in the combination.

2. Process for the vulcanisation of rubber substantially as hereinbefore described.

3. Vulcanised rubber whenever produced by a process claimed in either of the preceding claims.

Dated the 12th day of December, 1940.
E. A. BINGEN,
Solicitor for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1942.